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(74) Agents: GIBSON, Sara, Hillary, Margaret et al.; Intel-
lectual Property Department, Johnson Matthey Catalysts,
P.O. Box 1 Belasis Avenue, Billingham, Cleveland TS23
1LB (GB).

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(71) Applicant (*for all designated States except US*): JOHN-
SON MATTHEY PLC [GB/GB]; 2-4 Cockspur Street,
Trafalgar Square, London SW1Y 5BQ (GB).

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): STENGEL, Bruno,
Frederic [FR/GB]; 3 Prestwick Court, Eaglescliffe,
Stockton on Tees, Cleveland TS16 9ED (GB). SLACK,
Neville [GB/GB]; 139 Station Road, Billingham, Stock-
ton-on-Tees, Cleveland TS23 2RL (GB). PARTRIDGE,
Martin, Graham [GB/GB]; 33 Houghton Banks, Ingleby
Barwick, Stockton-on-Tees, Cleveland TS17 5AL (GB).

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(54) Title: ORGANOMETALLIC CATALYST COMPOSITION AND PROCESS FOR POLYURETHANE MANUFACTURE US-
ING SAID CATALYST

(57) Abstract: A catalyst composition comprises the reaction product of an alkoxide or condensed alkoxide of titanium, zirconium,
hafnium, aluminium, iron (III), or a lanthanide, a 2-hydroxy carboxylic acid, a base and optionally an alcohol containing at least two
hydroxyl groups. A process for the manufacture of polyurethane materials using the catalyst is also described.



WO 2004/050734 A1

ORGANOMETALLIC CATALYST COMPOSITION AND PROCESS FOR POLYURETHANE MANUFACTURE
USING SAID CATALYSTCatalyst and Process

The invention concerns a novel organometallic catalyst which is particularly suitable for use in the manufacture of polyurethane materials and also processes for the manufacture of polyurethanes using the organometallic catalysts.

Catalysts comprising compounds of titanium or zirconium are well known for use in many applications such as in esterification reactions and for curing reaction mixtures containing isocyanate and hydroxylic species to form polyurethanes. Typically, such catalysts comprise a metal alkoxide, such as titanium tetra isopropoxide, or a chelated species derived from the alkoxides.

In polyurethane manufacture the catalysts of choice in many applications have, for many years, been organic mercury and tin compounds. This is because these catalysts provide a desirable reaction profile which offers an initial induction period in which the reaction is either very slow or does not take place, followed by a rapid reaction which continues for sufficient time to produce a relatively hard polymer article. The induction time, also known as the "cream time", is desirable because it allows the liquid reaction mixture to be poured or moulded after addition of the catalyst and therefore gives the manufacturer more control over the manufacturing process. The rapid and complete reaction after the cream time is important to provide finished articles which are not sticky and which develop their desired physical properties quickly to allow fast turnaround in the production facility.

It is, however, known that mercury compounds are toxic and so there is a need for catalysts which do not contain mercury and yet which offer the manufacturer the desirable reaction profile which is offered by the known mercury-containing catalysts. Tin catalysts, such as dibutyltin dilaurate, are used extensively in polyurethane manufacture and are especially widely used in the manufacture of polyurethane foam articles. However, there are some concerns about the use of tin catalysts, especially in applications where people are exposed to the finished article for long periods, e.g. in furniture foam or shoe soles, because they may contain undesirable alkyl tin impurities. Although titanium alkoxides provide very effective catalysts for polyurethane cure reactions, they do not produce a reaction profile with the desirable cream time and cure profile described above. In many cases the reaction may be very rapid but offers no induction period and so the polyurethane mixture tends to gel very quickly, often before it can be cast into its final shape. A further problem is that, despite the rapid initial reaction, the resulting polyurethane does not achieve a satisfactory degree of cure within a reasonable time. This results in finished articles which are sticky and difficult to handle and which may have inferior physical properties compared with articles made using a mercury catalyst.

It is an object of the invention to provide a catalyst compound which does not contain mercury and which may be used to manufacture polyurethane articles. It is a further object of the invention to provide a catalyst which is stable in contact with water so that it may be used in polyurethane compositions and reactant formulations intended for polyurethane foams which often contain water as a blowing agent.

Monoalkoxytitanates such as titanium monoisopropoxy tris(isostearate) are well known for use as coupling agents between inorganic materials and organic polymeric materials. For example US-A-4397983 discloses the use of isopropyl tri(dodecylbenzenesulfonyl) titanate and isopropyl tri(dioctylphosphato) titanate for coupling fillers in polyurethanes.

US-A-4122062 describes organotitanates having one of the following formulas:

a) $(RO)_z Ti(A)_x (B)_y$ or

b) $(RO)Ti(OCOR')_p(OAr)_q$ wherein R is a monovalent alkyl, alkenyl, alkynyl, or aralkyl group having from 1 to 30 carbon atoms or substituted derivatives thereof; A is a thioaroxy, sulfonyl, sulfinyl, diester pyrophosphate, diester phosphate, or a substituted derivative thereof; OAr is aroxy; B is OCOR' or OAr; R' is hydrogen or a monovalent organic group having from 1 to 100 carbon atoms; $x+y+z$ equal 4; $p+q$ equal 3; x, z and q may be 1, 2 or 3; and y and p may be 0, 1 or 2; the reaction products of such organo-titanates and comminuted inorganic material; and polymeric materials containing such reaction products

US-A-4094853 describes a composition of matter comprising the reaction product of a comminuted inorganic material and an organo-titanate having the formula $(RO)Ti(OCOR')_3$ wherein R is a monovalent alkyl, alkenyl, alkynyl or aralkyl group having from 1 to 30 carbon atoms or a substituted derivative thereof, R' is a monovalent organic group the total number of carbon atoms in the three R' groups in a molecule being not more than 14; and polymeric materials containing such reaction products.

EP-A-0164227 describes neoalkoxy compounds having the formula

$R R^1 R^2 CCH_2OM(A)_a(B)_b(C)_c$ wherein M is titanium or zirconium, R, R¹ and R² are each a monovalent alkyl, alkenyl, alkynyl, aralkyl, aryl or alkaryl group having up to twenty carbon atoms or a halogen or ether substituted derivative thereof, and, in addition, R² may also be an oxy derivative or an ether substituted oxy derivative of said groups; A, B, and C are each a monovalent aroxy, thioaroxy, diester phosphate, diester pyrophosphate, oxyalkylamino, sulfonyl or carboxyl containing up to 30 carbon atoms; and $a + b + c = 3$. The compound is useful as a coupling and polymer processing agent and compositions containing the compound and methods of preparing polymeric material including the compound are also described.

GB-A-1509283 describes novel organo-titanates represented by the formula:

$Ti(OR)_{4-n}(OCOR')_n$ where OR is a hydrolyzable group; R' is a non-hydrolyzable group; and n is between about 3.0 and 3.50, preferably from 3.1 to 3.25. R, may be a straight chain, branched or cyclic alkyl group having from 1 to 5 carbon atoms per molecule. The non-hydrolyzable groups (OCOR') are preferably formed from organic acids having 6 to 24 carbon atoms, such as stearic, isostearic, oleic, linoleic, palmitic, lauric and tall oil acids.

The compounds are used for treating inorganic solids to improve the dispersion of the inorganic solids in polymeric compounds and to improve the physical properties of the filled polymeric compounds, i.e. the organo-titanates are used as coupling agents.

Monte and Sugerman (Journal of Cellular Plastics, November-December 1985, p385) describe the use of various neoalkoxytitanates and neoalkoxyzirconates as coupling agents in different polymer systems. They conclude that certain of the compounds are capable of directly catalysing the polyol-isocyanate reaction in addition to bonding polymer to substrate.

US-A-2846408 describes a process for preparing cellular polyurethane plastics of specified pore structure using metallic compounds defined by the general formula $Me(OR)_mX_{n-m}$ where R is alkyl and X is an organic carboxylic acid radical including lauric, stearic, palmitic, naphthenic and phenylacetic acids, m is at least 1 and n is the valence of the metal Me. Me includes titanium, zirconium and tin.

US-A-2926148 describes catalysts for the reaction between a diisocyanate and a mixture of alcohols to form resins. The catalysts include, apart from tin compounds, tetralkyl titanates and zirconates and various titanium esters which include triethanolamine titanate-N-stearate, triethanolamine titanate-N-oleate, octylene glycol titanate and triethanolamine titanate.

US-A-6133404 describes the use of monoalkoxytitanates as additives useful in the preparation of biodegradable polyester compositions.

US-A-5591800 describes the manufacture of polyesters using a cyclic titanium catalyst such as a titanate compound formed by the reaction of a tetra-alkyl titanate and a triol.

US-A-5,902,835 describes titanium, zirconium or hafnium blowing catalyst compositions for the production of polyurethane foams in which the blowing catalyst is a compound represented by the following formulae: $[M(L1)(L2)(L3)(L4)]_n$, $[M(L1)(L2)(L3)]_n$, $[M(L1)(L2)]_n$, $[M(L1)]_n$ wherein M is titanium, zirconium, or hafnium; n ranges from 1 to 20; and each of L1, L2, L3, and L4 is the same or different ligand selected from the following groups: (1) oxygen, sulfur and nitrogen; (2) an alcoholate,

phenolate, glycolate, thiolate, carboxylate, dithiocarbamate, aminate, aminoalcoholate, phosphate, phosphonate, pyrophosphate, sulfonate, or silylamide any of which contains from 1 to 20 carbon atoms and, optionally, contains one or more functional groups, or oxygen, sulfur, nitrogen, or phosphorus-containing; (3) a chelating ligand, such as, various non-fluorine containing and non-sterically hindered beta -diketones, triethanolamine, salicylaldehyde, and salicylamide.

In GB-A-2314081, an esterification catalyst comprising the reaction product of an alkoxide or condensed alkoxide of titanium or zirconium, an alcohol containing at least two hydroxyl groups, a 2-hydroxy carboxylic acid and a base. In that patent, the preferred amount of base for monobasic 2-hydroxy acids such as lactic acid, is in the range 0.8 to 1.2 mole per mole of 2-hydroxy acid. In the case of citric acid (a tribasic acid), the preferred amount is in the range 1 to 3 moles base per mole of 2-hydroxy acid. We have found that when a catalyst composition of the type described in GB-A-2314081 is made using 1,4-butane diol as the dihydric alcohol and an inorganic base is present in the preferred concentration range, the 1,4-butane diol forms a complex with the base leading to formation of a gelled product which is not suitable for use as a catalyst.

According to the invention we therefore provide a catalyst composition comprising the reaction product of an alkoxide or condensed alkoxide of titanium, zirconium, hafnium, aluminium, iron (III), or a lanthanide, a 2-hydroxy carboxylic acid, a base and optionally an alcohol containing at least two hydroxyl groups.

According to a further aspect of the invention, we also provide a composition comprising:

a) either

- i) a compound having more than one hydroxy group which is capable of reacting with an isocyanate group-containing material to form a polyurethane or
- ii) a compound having more than one isocyanate group which is capable of reacting with a hydroxyl group-containing material to form a polyurethane,

b) a catalyst composition comprising the reaction product of an alkoxide or condensed alkoxide of titanium, zirconium, hafnium, aluminium, iron (III), or a lanthanide, a 2-hydroxy carboxylic acid, a base and optionally an alcohol containing at least two hydroxyl groups; and optionally

c) one or more further components selected from chain modifiers, diluents, flame retardants, blowing agents, release agents, water, coupling agents, lignocellulosic preserving agents, fungicides, waxes, sizing agents, fillers, colourants, impact modifiers, surfactants, thixotropic agents, flame retardants, plasticisers, and other binders.

According to a further aspect of the invention, we also provide a process for the manufacture of a polyurethane article, comprising the steps of :

a) forming a mixture by mixing together either

- i) a compound having more than one hydroxy group which is capable of reacting with an isocyanate group -containing material to form a polyurethane or
- ii) a compound having more than one isocyanate group which is capable of reacting with a hydroxyl group-containing material to form a polyurethane,

with a catalyst composition comprising the reaction product of an alkoxide or condensed alkoxide of titanium, zirconium, hafnium, aluminium, iron (III), or a lanthanide; a 2-hydroxy carboxylic acid, a base and optionally an alcohol containing at least two hydroxyl groups;

b) adding to said mixture the other of the compound in a)i) or a) ii) which is not already present in the mixture,

c) forming said mixture into the required shape for the polyurethane article,

d) allowing said mixture to cure

e) optionally subjecting the mixture to specified conditions for post-cure conditioning.

15 The compound having more than one hydroxy group which is capable of reacting with an isocyanate group -containing material to form a polyurethane or the compound having more than one isocyanate group which is capable of reacting with a hydroxyl group-containing material to form a polyurethane may comprise a mixture of such compounds or a mixture of such compounds with different compounds, e.g. fillers or other additives etc. In particular, where the polyurethane article is intended to form a foam, the mixture of polyol or isocyanate may or of the two together may contain a blowing agent or a blowing catalyst to catalyse the reaction between isocyanate and water which generates carbon dioxide to form the foam. Suitable blowing catalysts include amines, in particular tertiary amines.

25 The catalyst of the invention is the reaction product of an alkoxide or condensed alkoxide of titanium, zirconium, hafnium, aluminium, iron (III), or a lanthanide, an alcohol containing at least two hydroxyl groups, a 2-hydroxy carboxylic acid and a base. Preferably, the alkoxide has the formula $M(OR)_x$ in which M is titanium, zirconium, hafnium, aluminium, iron (III) or a lanthanide, R is an alkyl group and x is the valency of the metal M. More preferably R contains 1 to 6 carbon atoms and particularly suitable alkoxides include tetraisopropoxy titanium, tetra-n-butoxy titanium, tetra-n-propoxy zirconium and tetra-n-butoxy zirconium, aluminium tri-sec-butoxide.

35 The condensed alkoxides suitable for preparing the catalysts useful in this invention are typically prepared by careful hydrolysis of titanium or zirconium alkoxides and are frequently represented by the formula $R^1O[M(OR^1)_2O]_nR^1$ in which R^1 represents an alkyl group and M represents titanium or zirconium. Preferably, n is less than 20 and more preferably is less than 10. Preferably R^1 contains

1 to 6 carbon atoms and useful condensed alkoxides include the compounds known as polybutyl titanate, polyisopropyl titanate and polybutyl zirconate.

Preferred 2-hydroxy carboxylic acids include lactic acid, citric acid, malic acid and tartaric acid.

- 5 Aromatic acids such as mandelic acid may also be used. Some suitable acids are supplied as salts, hydrates or as aqueous mixtures. Acids in this form as well as anhydrous acids are suitable for preparing the catalysts used in this invention. Preferably the catalyst contains 1 to 4 moles (more preferably 1.5 to 3.5 moles) of 2-hydroxy acid per mole of titanium, zirconium, hafnium, aluminium, iron (III), or lanthanide.

10

The base used in preparing the catalyst composition is generally an inorganic base and suitable bases include aqueous solutions of salts of weak acids with metals selected from Group IA or IIA of the periodic table of elements or with zinc, aluminium, iron(II), copper(II), nickel, cobalt (II), manganese (II), lanthanum, cerium, neodymium, and samarium. Preferred bases include sodium
15 hydroxide, potassium hydroxide, ammonium hydroxide, lithium hydroxide, sodium carbonate, magnesium hydroxide, calcium hydroxide, aluminium acetate, zinc oxide, caesium carbonate, zirconium hydroxycarbonate and ammonia. The molar ratio of base to 2-hydroxy carboxylic acid is preferably in the range 0.05 to 1.5 : 1 and more preferably in the range 0.1 to 1.2 : 1, although if a more basic composition is required then more base may be used. Where the 2-hydroxy acid
20 contains more than one carboxylic acid group, such as in citric acid for example, the preferred molar ratios given are per mole equivalent of carboxylic acid functionality. In general, the amount of base present is usually in the range 0.05 to 12 moles (preferably from 0.5 to 4) per mole of titanium, zirconium, hafnium, aluminium, iron (III), or lanthanide.

- 25 Preferably the alcohol containing at least two hydroxyl groups is a dihydric alcohol e.g. 1,2-ethanediol, 1,2-propanediol, 1,3-propanediol, 1,4-butane diol or a dihydric alcohol containing a longer chain such as diethylene glycol or a polyethylene glycol. The catalyst can also be prepared from a polyhydric alcohol such as glycerol, trimethylolpropane or pentaerythritol. The presence of the alcohol is optional but in preferred compositions, the alcohol is present. When present, the
30 alcohol provides a liquid composition which is easily handled as a polyurethane catalyst. When the alcohol is not present, a liquid composition may be obtained through the addition of water. Preferably the catalyst is prepared by reacting a dihydric alcohol with an alkoxide or condensed alkoxide in a ratio of from 2 to 12 moles (more preferably 4 to 8 moles) of dihydric alcohol to each mole of the titanium, zirconium, hafnium, aluminium, iron (III), or lanthanide.

35

It is frequently convenient to add water together with the base when preparing the catalysts.

The catalyst can be prepared by mixing the components (alkoxide or condensed alkoxide, dihydric alcohol or water (if used), 2-hydroxy acid and base) with removal of any by-product, (e.g. isopropyl alcohol when the alkoxide is tetraisopropoxytitanium), at any appropriate stage. In one preferred method the alkoxide or condensed alkoxide and dihydric alcohol are mixed and subsequently, 2-hydroxy acid and then base (or a pre-neutralised 2-hydroxy acid solution), is added. In an alternative preferred method the alkoxide or condensed alkoxide is reacted with the 2-hydroxy acid and by-product alcohol is removed. Base is then added to this reaction product followed by a dihydric alcohol or water to produce the reaction product which is a catalyst in the process of the invention. If desired, further by-product alcohol can then be removed by distillation. An aqueous solution of the 2-hydroxy acid or a salt thereof may be used. The catalyst may be diluted in a solvent, which may be an alcohol or water, for example a compound which is to be used in the polyurethane reaction. As an example the solvent may be a diol such as 1,4-butanediol which is often used as a chain extender in commercial polyol compositions supplied for polyurethane manufacture.

The compound of the invention is particularly useful as a cure catalyst for the reaction between a hydroxy-functionalised molecule, such as a polyol, and an isocyanate-functionalised molecule, such as a polyisocyanate. This reaction forms the basis of many commercially available two-component polyurethane systems. The polyol component may be any suitable for the manufacture of polyurethanes and includes polyester-polyols, polyester-amide polyols, polyether-polyols, polythioetherpolyols, polycarbonate polyols, polyacetal polyols, polyolefin polyols polysiloxane polyols, dispersions or solutions of addition or condensation polymers in polyols of the types described above, often referred to as "polymer" polyols. A very wide variety of polyols has been described in the prior art and is well known to the formulator of polyurethane materials.

Typically, a mixture of polyols is used to manufacture polyurethane having particular physical properties. The polyol or polyols is selected to have a molecular weight, backbone type and hydroxy functionality which is tailored to the requirements of the formulator. Typically the polyol includes a chain extender, which is often a relatively short-chain diol such as 1,4-butane diol or diethylene glycol or a low molecular weight polyethylene glycol. Alternative chain extenders in commercial use, such as diamines, e.g. MOCA (4,4-methylene bis (2-chloroaniline)) may also be used.

The isocyanate compositions used for polyurethane manufacture suitable for use with the catalysts of the present invention may be any organic polyisocyanate compound or mixture of organic polyisocyanate compounds which are commercially useful for the purpose. Suitable organic polyisocyanates include diisocyanates, particularly aromatic diisocyanates, and isocyanates of higher functionality. Examples of suitable organic polyisocyanates include aliphatic isocyanates such

as hexamethylene diisocyanate and isophorone diisocyanate; and aromatic isocyanates such as m- and p-phenylene diisocyanate, tolylene-2,4- and tolylene- 2,6-diisocyanate, diphenylmethane-4,4'-diisocyanate, chlorophenylene- 2,4-diisocyanate, naphthylene-1,5-diisocyanate, diphenylene-4,4'-diisocyanate, 4,4'-diisocyanate-3,3'-dimethyl-diphenyl, 3-methyldiphenylmethane-4,4'-di-isocyanate and diphenyl ether diisocyanate; and cycloaliphatic diisocyanates such as cyclohexane-2,4- and -2,3-diisocyanate, 1-methylcyclohexyl-2,4- and -2,6-diisocyanate and mixtures thereof and bis-(isocyanatocyclohexyl)methane and triisocyanates such as 2,4,6-triisocyanatotoluene and 2,4,4-tri-isocyanatodiphenylether.

Modified polyisocyanates containing isocyanurate, carbodiimide or uretonimine groups may be used. The polyisocyanate may also be an isocyanate-ended prepolymer made by reacting an excess of a diisocyanate or higher functionality polyisocyanate with a polyol for example a polyether polyol or a polyester polyol. The use of prepolymers is common in commercially available polyurethane systems. In these cases, polyols may already be incorporated in the isocyanate or prepolymer whilst further components such as chain extenders, polyols etc may be mixed with the isocyanate prepolymer mixture before polymerisation.

Mixtures of isocyanates may be used in conjunction with the organometallic composition of the invention, for example a mixture of tolylene diisocyanate isomers such as the commercially available mixtures of 2,4- and 2,6-isomers. A mixture of di- and higher polyisocyanates, such as trimers (isocyanurates) or pre-polymers, may also be used. Polyisocyanate mixtures may optionally contain monofunctional isocyanates such as p-ethyl phenylisocyanate.

Preferably the polyisocyanate is liquid at room temperature.

The organometallic composition of the invention is typically added to the polyol prior to mixing together the polyol component with the isocyanate component to form the polyurethane. However, the organometallic composition may instead be added to the isocyanate component if required.

A composition containing a catalyst composition of the present invention and a polyisocyanate and compounds reactive therewith may further comprise conventional additives such as chain modifiers, diluents, flame retardants, blowing agents, release agents, water, coupling agents, lignocellulosic preserving agents, fungicides, waxes, sizing agents, fillers, colourants, impact modifiers, surfactants, thixotropic agents, flame retardants, plasticisers, and other binders. The selection of these and other ingredients for inclusion in a formulation for a polyurethane composition is well known to the skilled person and may be selected for the particular purpose.

When the mixture has been allowed to cure it may be further conditioned to allow for post-cure. Typically this occurs when the polyurethane article, coating etc has hardened to a state in which it may be handled, de-moulded etc and then it may be held at elevated temperature, e.g. by placing in an oven, to develop or enhance the full cured properties of the article.

The catalysts of the present invention are useful for the manufacture of polyurethane foams, flexible or rigid articles, coatings, adhesives, elastomers, sealants, thermoplastic polyurethanes, and binders e.g. for oriented strand board manufacture. The catalysts of the present invention may also be useful in preparing polyurethane prepolymers, i.e. urethane polymers of relatively low molecular weight which are supplied to end-users for curing into polyurethane articles or compositions of higher molecular weight.

The catalysts are typically present in the isocyanate and/or alcohol mixture to give a concentration in the range 1×10^{-4} to 10% by weight, preferably up to about 4% by weight based upon the weight of the total reaction system, i.e. the total weight of the polyisocyanate and polyol components.

The invention is illustrated by the following examples.

EXAMPLE 1

Water (52.25g, 2.90 moles) and citric acid monohydrate (75g, 0.36 moles) were placed into a pre-weighed rotary evaporator flask, and heated for 15 minutes to dissolve the citric acid. The solution was allowed to cool. A vacuum was applied to the flask and titanium (IV) n-butoxide (48.5g, 0.14 moles) (VERTEC™ TNBT) added via vacuum inlet. An azeotrope of n-butanol/water was removed under reduced pressure. The resulting mixture was allowed to cool before the dropwise addition of 5% magnesium hydroxide in water (145g, 0.125 moles). 1,4-butanediol (103 g, 1.14 moles) was then added dropwise, whilst stirring. An azeotrope of n-butanol/water was removed under reduced pressure. The resulting mixture was allowed to cool before 50% dilution with 1,4-butanediol to yield a slightly hazy solution with a titanium content of 1.54%.

EXAMPLE 2

Example 1 was repeated except that 5% lithium hydroxide in water (105g, 0.125 moles) was added in place of the magnesium hydroxide. The resulting mixture was allowed to cool before 50% dilution with 1,4-butanediol to yield a slightly hazy solution with a titanium content of 1.33%.

EXAMPLE 3

Example 1 was repeated except that 5% aluminium acetate $((\text{CH}_3\text{CO}_2)_2\text{AlOH})$ in water (408g, 0.125 moles) was added in place of the magnesium hydroxide. The resulting mixture was allowed to cool

before 50% dilution with 1,4-butanediol to yield a slightly hazy solution with a titanium content of 1.84%.

EXAMPLE 3A

- 5 Example 3 was repeated using a 10% aqueous solution of aluminium acetate to make a higher pH composition.

EXAMPLE 4

- 10 Example 1 was repeated except that 5% zinc oxide in water (203, 0.125 moles) was added in place of the magnesium hydroxide. The resulting mixture was allowed to cool before 50% dilution with 1,4-butanediol to yield a slightly hazy solution with a titanium content of 2.10%.

EXAMPLE 5

- 15 Example 1 was repeated except that 5% caesium carbonate in water (407g, 0.125 moles) was added in place of the magnesium hydroxide. The resulting mixture was allowed to cool before 50% dilution with 1,4-butanediol to yield a slightly hazy solution with a titanium content of 1.71%.

EXAMPLE 6

- 20 50% Citric acid solution (0.18mole, 69.12g) was taken in a rotary evaporator flask to which aluminium tri-sec-butoxide (0.0639mole, 15.75g) was added dropwise from a dropping funnel. On stirring it dissolved giving a cloudy suspension (slightly exothermic). The mixture was distilled under vacuum at 80°C for nearly 2 hours to remove water and butanol. 50g (0.0625 mole) of a 5% (by wt) aqueous NaOH solution was added dropwise followed by 1,4 butanediol (0.57mole, 51.375g). The remaining butanol and water were removed at 110°C under vacuum.

EXAMPLE 7

Example 6 was repeated with the exception that 101.72g (0.0625 mole) of a 5% (by wt) aqueous ZnO solution was added instead of the NaOH solution.

EXAMPLE 8

- 30 385 g (3.76 mole) of 88% lactic acid was placed into weighed 2-litre fishbowl flask and 640 g de-mineralised water added. 534 g (1.88 mole) of tetra-(isopropoxy) titanium (VERTECTM TIPT) was slowly added to the stirred lactic acid solution over a period of about 30 minutes, and the temperature maintained below 40 °C. A hazy white suspension was produced which was then
35 refluxed at 85-90 °C for one hour. The mixture was allowed to cool before a still head and condenser were attached to the flask and the mixture maintained at 100 °C for 2-3 minutes to remove isopropanol. The mixture was again allowed to cool to room temperature before slow

addition of 288 g (3.76 mole) 28% ammonium hydroxide solution. The product contained 8.26% Ti (by weight) and had a specific gravity of 1.231 g/cm³.

EXAMPLE 9

5 426 g, 1.5 mole, TIPT was placed into a weighed 2 litre fishbowl flask, fitted with a stirrer, thermometer, condenser and lid. The flask was placed in a water bath and fitted with a weighed 500ml dropping funnel containing 648 g, (6 moles), diethylene glycol (DEG). The DEG was run slowly into the TIPT over a period of around 30 minutes, so that the temperature did not exceed 40 °C. The final mix was stirred for 5 minutes, to complete the reaction, and allowed to cool below 30 °C. 306.8 g 88% w/w lactic acid (3 mole) was slowly added to the mix, from a weighed 500 ml dropping funnel, and the temperature again maintained below 40 °C. The reaction flask was then fitted with a dip tube connected to a supply of ammonia gas and the mix was neutralized by bubbling ammonia gas through the stirred mix. The pH of the mix was taken at regular intervals using moistened 1-14 pH paper and the mix temperature maintained below 40 °C. The neutralized mix was transferred to a weighed Buchi flask, which was fitted to a rotary evaporator. The mix was then stripped to constant weight, at temperatures up to 85 °C, to remove 360 g IPA, (6 moles) and 37 g water (2 moles) (from the 88% lactic acid). The final stripped mix was a clear orange coloured liquid containing 6.89% Ti, and having a specific gravity of 1.260 g/cm³, a viscosity of 10.22 poise, a flash point of 115°C. The pH of 10% solution in water was between 5 and 6.

EXAMPLE 10

415 g (4.06 Mole) of 88% lactic acid was placed into weighed 2-litre fishbowl flask and 640 g de-mineralised water added. 534 g (1.88 mole) VERTECTM TIPT was slowly added to the stirred lactic acid solution over a period of about 30 minutes, and the temperature maintained below 40°C. A hazy white suspension was produced which was then refluxed at 85-90 °C for one hour. The mixture was allowed to cool before a still head and condenser were attached to the flask and the mixture maintained at 100 °C for 2-3 minutes to remove isopropanol. The flask was again cooled below 30°C and 30 g of zirconium carbonate hydroxide powder was gradually added into the stirred mix. Release of CO₂ occurred, causing effervescence and some foaming. The mix was stirred for a further 5 minutes, to give maximum dispersion and solution of the zirconium carbonate. The resulting mix was a hazy yellow-white colour. 100 ml of de-mineralised water was slowly added to the stirred mix, to try to dissolve the haziness, but with little effect, even after heating to 80°C. A further 100mls of water was again added, but the mix again remained hazy. Finally, 246 g (4.05 mole) 28% Ammonium hydroxide solution was slowly added. The mix became clear after addition of around 90% of the ammonia solution. The remaining ammonia was added and the mix stirred for 5 minutes to give complete dispersion.

The product contained 7.47% of Ti, 2.1 - 2.23 % of Zr, had a specific gravity of 1.226 g/cm³ and a pH (10% in water) of 8 - 9.

EXAMPLE 11

- 5 a) 220.6 g of citric acid monohydrate crystals was placed into weighed 1-litre fishbowl flask and 526.4 g de-mineralised water added. The temperature of the mix was raised to around 25°C to dissolve the citric acid. 106.5 g (0.375 mole) VERTECTM TIPT was added slowly into the stirred mix and the temperature maintained below 40°C. The resulting white suspension was refluxed at 85-90 °C for one hour to give a clear solution. The mix was cooled, before a still head and condenser were
10 attached to the flask, to enable distillation of iso-propanol and water. A thermometer was fitted into a still head and the mix heated to 100 °C, and maintained at this temperature for 2-3 minutes to remove all IPA.
- b) The flask was again allowed to cool to room temperature before addition of ammonia solution which was prepared by diluting 28% ammonia solution 1: 1 by weight. 61.5 g of this 1:1 w/w solution
15 (0.5 mole NH₃) was slowly run into the titanium citrate mix. The pH of the mix was raised from 1 to 2 during the ammonia addition.
- c) 78.6 g zinc citrate dihydrate (0.129 mole) was dissolved in a further 123.3 g of the prepared ammonia solution. This solution was slowly added to the stirred titanium-containing mixture (pH raised to about 3). A further 61.5 g of the ammonia solution was added to further increase the pH of
20 the mix to 4.

EXAMPLE 12

- The method of part a of Example 11 was repeated to make a titanium citrate solution, using 210.3 g (1.0 mole) of citric acid monohydrate crystals, 520 g of de-mineralised water, 142.0 g (0.5 mole) of
25 VERTECTM TIPT. About 120 g of diluted (1 : 1 w/w) ammonia solution (1 mole NH₃) was slowly added and the pH of the mix after this addition was around 4. A further 60.7g (1 mole) of 28% ammonium hydroxide solution was again diluted 1:1 w/w with water and added to the mix to further increase the pH. The mixture was made up with water to give a total weight of 1000g and filtered to give a clear solution containing 2.37% Ti and having a pH (10% solution) of 5 and a specific gravity
30 of 1.138 g/cm³.

EXAMPLE 13

- The method of part a of Example 4 was repeated to make a titanium citrate solution, using 480 g (1.25 mole) of a pre-mixed 50% citric acid solution, 300 g of de-mineralised water, 142.0 g (0.5
35 mole) of VERTECTM TIPT.
- After removal of IPA by distillation, the remaining mixture was cooled and neutralized with 76 g 28% ammonium hydroxide solution (1.25 mole NH₃) and then, 376 g (6.06 moles) of ethylene glycol was

added from a dropping funnel. The mixture was stirred for 5 minutes to give a homogeneous though slightly hazy mix having a pH of 4. 250 ml was removed for analysis and a further 88.3g ammonium hydroxide solution was added from a dropping funnel into the remaining mix (936 g), increasing the pH to 6. The Ti content was 1.87% and the SG 1.064 g/cm³.

EXAMPLE 14

The catalysts of the invention were used as catalysts in the preparation of polyurethane foams. All the catalysts were found to be hydrolytically stable.

50g of a commercial polyether polyol preparation containing an organic filler, surfactants, fillers, pigments, a tertiary amine (as blowing agent), 1,4-butane diol (chain extender) and water (for the foam blowing reaction) was placed in a disposable speed mixer cup. A measured amount of the appropriate catalyst (see Table 1) was added and the mixture was mixed at 3000rpm. 35g of 4,4'-methylenbis phenylisocyanate (MDI) based prepolymer (%NCO = 18.4) was added and the whole mixture was hand mixed for 20 seconds, then poured into a disposable beaker. A thin wire of (HI-92704C) K-thermocouple was inserted to record the exotherm of the foaming reaction. The foam height and cream time were recorded for each mixture.

The same preparation was carried out using a commercial tin catalyst as a comparison.

The density (g/l) of the foams was measured by weighing to determine the mass and using a water displacement method to determine the volume of the foam.

The results show that foams of at least comparable density to those produced using the tin catalyst were produced using the catalysts of the invention. The longer cream times are of benefit in some applications where time to mould the mixtures is required before the foam is formed. Some catalysts were mixed with the polyol and stored before use in order to determine the effect of storage in contact with polyol and water. The results show that the catalysts have a good shelf life.

In order to show the effect of the amine catalyst used, the preparations were repeated in the absence of the amine catalyst. The product polyurethane became gelled but the foams did not rise and the exotherms were low (<40 °C) indicating that the amine catalyst used functioned as the blowing catalyst, whilst the catalysts of the invention were functioning as gelation catalysts.

Table 1

Catalyst	Foam height(mm)	Amount of catalyst (g)	Cream time (mins)	Density(g/l)	Exotherm(°C)
Example 1	50	0.2	18-21	463	91
Example 2	56	0.2	18-21	416	98
Example 3	79	0.2	18-21	311	98
Example 4	60	0.2	18-21	388	95
Example 5	49	0.2	18-21	471	94
Example 6	60	0.2	20-25	353	98
Example 6	46	0.07	20-25	447	100
Example 7	47	0.07	20-25	475	100
Example 7	45	0.06	20-25	463	98
Example 8	52	0.055	20-22	299	98
Example 9	47	0.058	20-22	324	95
Example 10	41	0.055	20-22	383	93
Example 11	43	0.051	20-22	374	99
Example 12	45	0.054	20-22	342	91
Example 13	73	0.05	20-22	303	95
Tin (comparison)	53	0.2	18-21	399	95
Example 8*	79	0.055	20-22	234	97
Example 9*	55	0.054	20-22	380	97
Example 12*	67	0.05	20-22	322	100

* Catalyst mixed with polyol and stored for 8 days before addition of isocyanate.

Claims

1. A process for the manufacture of a polyurethane article, comprising the steps of :
 - a) forming a mixture by mixing together either
 - i) a compound having more than one hydroxy group which is capable of reacting with an isocyanate group -containing material to form a polyurethane or
 - ii) a compound having more than one isocyanate group which is capable of reacting with a hydroxyl group-containing material to form a polyurethane,
 - with a catalyst composition comprising the reaction product of an alkoxide or condensed alkoxide of titanium, zirconium, hafnium, aluminium, iron (III), or a lanthanide, a 2-hydroxy carboxylic acid, a base and optionally an alcohol containing at least two hydroxyl groups;
 - b) adding to said mixture the other of the compound having more than one hydroxy group which is capable of reacting with an isocyanate group -containing material to form a polyurethane or the a compound having more than one isocyanate group which is capable of reacting with a hydroxyl group-containing material to form a polyurethane,
 - c) forming said mixture into the required shape for the polyurethane article,
 - d) allowing said mixture to cure
 - e) optionally subjecting the mixture to specified conditions for post-cure conditioning.
2. A process as claimed in claim 1, wherein the polyurethane article is a foam and a blowing catalyst is added to the mixture formed in step a).
3. A process as claimed in claim 1 or claim 2, wherein in said catalyst composition, the alcohol is selected from the group consisting of 1,2-ethanediol, 1,2-propanediol, 1,3-propanediol, 1,4-butane diol, diethylene glycol and a polyethylene glycol.
4. A process as claimed in any of the preceding claims, wherein, in said catalyst composition, the 2-hydroxy carboxylic acid comprises lactic acid, citric acid, malic acid or tartaric acid.
5. A process as claimed in any of the preceding claims, wherein, in said catalyst composition, the molar ratio of acid to titanium or zirconium in the reaction product is from 1 to 4 moles acid per mole of titanium, zirconium, hafnium, aluminium, iron (III), or lanthanide.
6. A process as claimed in any of the preceding claims, wherein, in said catalyst composition, the base comprises sodium hydroxide, potassium hydroxide, ammonium hydroxide, lithium hydroxide, sodium carbonate, magnesium hydroxide, calcium hydroxide, aluminium acetate, zinc oxide, caesium carbonate, zirconium hydroxycarbonate or ammonia.

7. A composition comprising:

a) either

- i) a compound having more than one hydroxy group which is capable of reacting with an isocyanate group -containing material to form a polyurethane or
- ii) a compound having more than one isocyanate group which is capable of reacting with a hydroxyl group-containing material to form a polyurethane,

- b) a catalyst composition comprising the reaction product of an alkoxide or condensed alkoxide of titanium, zirconium, hafnium, aluminium, iron (III), or a lanthanide, a 2-hydroxy carboxylic acid, a base and optionally an alcohol containing at least two hydroxyl groups; and optionally
- c) one or more further components selected from chain modifiers, diluents, flame retardants, blowing agents, release agents, water, coupling agents, lignocellulosic preserving agents, fungicides, waxes, sizing agents, fillers, colourants, impact modifiers, surfactants, thixotropic agents, flame retardants, plasticisers, and other binders.

8. A catalyst composition comprising the reaction product of an alkoxide or condensed alkoxide of titanium, zirconium, hafnium, aluminium, iron (III), or a lanthanide, a 2-hydroxy carboxylic acid, a base and optionally an alcohol containing at least two hydroxyl groups.

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A. CLASSIFICATION OF SUBJECT MATTER IPC 7 C08G18/22 B01J31/38		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 7 C08G B01J		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	WO 02 096968 A (ICI PLC ; STENGEL BRUNO FREDERIC (GB)) 5 December 2002 (2002-12-05) page 2, line 34 -page 3, line 10 page 5, line 6 -page 5, line 20 claims 1,3,8	7,8
X	EP 1 120 392 A (ACMA LTD) 1 August 2001 (2001-08-01) paragraphs '0015!-'0019!; claims 1,7,8,11,14	8
A	WO 98 15585 A (TIOXIDE SPECIALTIES LTD ;RIDLAND JOHN (GB); SKINNER CHRISTOPHER JO) 16 April 1998 (1998-04-16) examples 1,4,6 claims 1-3,6	1-7
-/--		
<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C.		
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* Special categories of cited documents : *A* document defining the general state of the art which is not considered to be of particular relevance *E* earlier document but published on or after the international filing date *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) *O* document referring to an oral disclosure, use, exhibition or other means *P* document published prior to the international filing date but later than the priority date claimed *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. *Z* document member of the same patent family		
Date of the actual completion of the international search 27 February 2004		Date of mailing of the international search report 08/03/2004
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer Heidenhain, R

INTERNATIONAL SEARCH REPORT

Intern: Application No
PCT/GB 03/05182

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 01 51536 A (PARTRIDGE MARTIN GRAHAM ; ICI PLC (GB); RIDLAND JOHN (GB); STENGEL) 19 July 2001 (2001-07-19) claims 1, 8-10, 16, 17 ---	1-7
A	WO 98 41322 A (KING INDUSTRIES INC) 24 September 1998 (1998-09-24) page 3, line 33 -page 4, line 33 example 2 table III claims 1-5 -----	1-7

INTERNATIONAL SEARCH REPORT

Internation application No
PCT/GB 03/05182

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 02096968	A	05-12-2002	CA 2448200 A1 WO 02096968 A1	05-12-2002 05-12-2002
EP 1120392	A	01-08-2001	EP 1120392 A1 AT 254096 T AT 207866 T AU 730131 B2 AU 2363597 A BR 9703577 A CA 2207111 A1 CN 1169412 A ,B CZ 9701762 A3 DE 69707757 D1 DE 69707757 T2 DE 69726200 D1 DK 812818 T3 EP 0812818 A1 ES 2166505 T3 GB 2314081 A ,B HU 9701024 A2 JP 10081646 A NO 972645 A PL 320469 A1 PT 812818 T RU 2178783 C2 TR 9700487 A2 US 5866710 A	01-08-2001 15-11-2003 15-11-2001 22-02-2001 18-12-1997 10-11-1998 11-12-1997 07-01-1998 13-05-1998 06-12-2001 25-04-2002 18-12-2003 19-11-2001 17-12-1997 16-04-2002 17-12-1997 02-03-1998 31-03-1998 12-12-1997 22-12-1997 28-02-2002 27-01-2002 21-12-1997 02-02-1999
WO 9815585	A	16-04-1998	AU 735671 B2 AU 4312697 A BR 9711862 A CA 2267773 A1 CN 1239484 A CZ 9901180 A3 EP 0929585 A1 WO 9815585 A1 HU 0000438 A2 ID 17410 A JP 2001501534 T KR 2000048918 A NO 991616 A NZ 335210 A PL 332641 A1 TR 9901203 T2 TW 394782 B ZA 9708667 A	12-07-2001 05-05-1998 28-08-2001 16-04-1998 22-12-1999 15-09-1999 21-07-1999 16-04-1998 28-06-2000 24-12-1997 06-02-2001 25-07-2000 04-06-1999 28-01-2000 27-09-1999 23-08-1999 21-06-2000 06-04-1998
WO 0151536	A	19-07-2001	AU 2201001 A CA 2395577 A1 CN 1423667 T EP 1252214 A1 WO 0151536 A1 JP 2003519631 T	24-07-2001 19-07-2001 11-06-2003 30-10-2002 19-07-2001 24-06-2003
WO 9841322	A	24-09-1998	US 5846897 A AT 258825 T AU 729058 B2 AU 6555098 A	08-12-1998 15-02-2004 25-01-2001 12-10-1998

INTERNATIONAL SEARCH REPORT

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PCT, JJ 03/05182

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9841322	A	CA 2266886 A1	24-09-1998
		DE 1021245 T1	19-04-2001
		EP 1163956 A1	19-12-2001
		EP 1021245 A1	26-07-2000
		JP 2001524142 T	27-11-2001
		WO 9841322 A1	24-09-1998
		US 5965686 A	12-10-1999

AMENDED CLAIMS

[received by the International Bureau on 13 April 2004 (13.04.04); original claims 1,7-8 amended; claim 9 added; remaining claims unchanged (3 pages)]

1. A process for the manufacture of a polyurethane article, comprising the steps of :
 - a) forming a mixture by mixing together either
 - a compound having more than one hydroxy group which is capable of reacting with an isocyanate group -containing material to form a polyurethane
 - or
 - a compound having more than one isocyanate group which is capable of reacting with a hydroxyl group-containing material to form a polyurethane,with a catalyst composition comprising the reaction product of:
 - i. an alkoxide or condensed alkoxide of titanium, zirconium, hafnium, aluminium, iron (III), or a lanthanide,
 - ii. a 2-hydroxy carboxylic acid,
 - iii. a base and
 - iv. optionally an alcohol containing at least two hydroxyl groups;
 - b) adding to said mixture the other of the compound having more than one hydroxy group which is capable of reacting with an isocyanate group -containing material to form a polyurethane or the a compound having more than one isocyanate group which is capable of reacting with a hydroxyl group-containing material to form a polyurethane,
 - c) forming said mixture into the required shape for the polyurethane article,
 - d) allowing said mixture to cure
 - e) optionally subjecting the mixture to specified conditions for post-cure conditioning.
2. A process as claimed in claim 1, wherein the polyurethane article is a foam and a blowing catalyst is added to the mixture formed in step a).
3. A process as claimed in claim 1 or claim 2, wherein in said catalyst composition, the alcohol is selected from the group consisting of 1,2-ethanediol, 1,2-propanediol, 1,3-propanediol, 1,4-butane diol, diethylene glycol and a polyethylene glycol.
4. A process as claimed in any of the preceding claims, wherein, in said catalyst composition, the 2-hydroxy carboxylic acid comprises lactic acid, citric acid, malic acid or tartaric acid.

5. A process as claimed in any of the preceding claims, wherein, in said catalyst composition, the molar ratio of acid to titanium or zirconium in the reaction product is from 1 to 4 moles acid per mole of titanium, zirconium, hafnium, aluminium, iron (III), or lanthanide.
6. A process as claimed in any of the preceding claims, wherein, in said catalyst composition, the base comprises sodium hydroxide, potassium hydroxide, ammonium hydroxide, lithium hydroxide, sodium carbonate, magnesium hydroxide, calcium hydroxide, aluminium acetate, zinc oxide, caesium carbonate, zirconium hydroxycarbonate or ammonia.
7. A composition comprising:
 - a) either
 - i) a compound having more than one hydroxy group which is capable of reacting with an isocyanate group-containing material to form a polyurethane or
 - ii) a compound having more than one isocyanate group which is capable of reacting with a hydroxyl group-containing material to form a polyurethane, and
 - b) a catalyst composition comprising the reaction product of:
 - i. an alkoxide or condensed alkoxide of titanium, zirconium, hafnium, aluminium, iron (III), or a lanthanide,
 - ii. a 2-hydroxy carboxylic acid,
 - iii. a base and
 - iv. optionally an alcohol containing at least two hydroxyl groups;and optionally
 - c) one or more further components selected from chain modifiers, diluents, flame retardants, blowing agents, release agents, water, coupling agents, lignocellulosic preserving agents, fungicides, waxes, sizing agents, fillers, colourants, impact modifiers, surfactants, thixotropic agents, flame retardants, plasticisers, and other binders.
8. A catalyst composition comprising the reaction product of:

- i. an alkoxide or condensed alkoxide of titanium, zirconium, hafnium, aluminium, iron (III), or a lanthanide,
- ii. a 2-hydroxy carboxylic acid,
- iii. a base and
- iv. optionally an alcohol containing at least two hydroxyl groups.

9. A catalyst composition as claimed in claim 8, wherein component i) is an alkoxide or condensed alkoxide of aluminium, iron (III), or a lanthanide.

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Minimum documentation searched (classification system followed by classification symbols)
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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

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P, X	WO 02 096968 A (ICI PLC ; STENGEL BRUNO FREDERIC (GB)) 5 December 2002 (2002-12-05) page 2, line 34 -page 3, line 10 page 5, line 6 -page 5, line 20 claims 1,3,8	7,8
X	EP 1 120 392 A (ACMA LTD) 1 August 2001 (2001-08-01) paragraphs '0015!-'0019!; claims 1,7,8,11,14	8
A	WO 98 15585 A (TIOXIDE SPECIALTIES LTD ;RIDLAND JOHN (GB); SKINNER CHRISTOPHER JO) 16 April 1998 (1998-04-16) examples 1,4,6 claims 1-3,6	1-7
	--- -/--	

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☒ Patent family members are listed in annex.

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Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Heidenhain, R

INTERNATIONAL SEARCH REPORT

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PCT/au 03/05182

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 01 51536 A (PARTRIDGE MARTIN GRAHAM ; ICI PLC (GB); RIDLAND JOHN (GB); STENGEL) 19 July 2001 (2001-07-19) claims 1, 8-10, 16, 17 ---	1-7
A	WO 98 41322 A (KING INDUSTRIES INC) 24 September 1998 (1998-09-24) page 3, line 33 -page 4, line 33 example 2 table III claims 1-5 -----	1-7

INTERNATIONAL SEARCH REPORT

Internals application No
PCT/US 03/05182

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 02096968	A	05-12-2002	CA 2448200 A1 WO 02096968 A1	05-12-2002 05-12-2002
EP 1120392	A	01-08-2001	EP 1120392 A1 AT 254096 T AT 207866 T AU 730131 B2 AU 2363597 A BR 9703577 A CA 2207111 A1 CN 1169412 A , B CZ 9701762 A3 DE 69707757 D1 DE 69707757 T2 DE 69726200 D1 DK 812818 T3 EP 0812818 A1 ES 2166505 T3 GB 2314081 A , B HU 9701024 A2 JP 10081646 A NO 972645 A PL 320469 A1 PT 812818 T RU 2178783 C2 TR 9700487 A2 US 5866710 A	01-08-2001 15-11-2003 15-11-2001 22-02-2001 18-12-1997 10-11-1998 11-12-1997 07-01-1998 13-05-1998 06-12-2001 25-04-2002 18-12-2003 19-11-2001 17-12-1997 16-04-2002 17-12-1997 02-03-1998 31-03-1998 12-12-1997 22-12-1997 28-02-2002 27-01-2002 21-12-1997 02-02-1999
WO 9815585	A	16-04-1998	AU 735671 B2 AU 4312697 A BR 9711862 A CA 2267773 A1 CN 1239484 A CZ 9901180 A3 EP 0929585 A1 WO 9815585 A1 HU 0000438 A2 ID 17410 A JP 2001501534 T KR 2000048918 A NO 991616 A NZ 335210 A PL 332641 A1 TR 9901203 T2 TW 394782 B ZA 9708667 A	12-07-2001 05-05-1998 28-08-2001 16-04-1998 22-12-1999 15-09-1999 21-07-1999 16-04-1998 28-06-2000 24-12-1997 06-02-2001 25-07-2000 04-06-1999 28-01-2000 27-09-1999 23-08-1999 21-06-2000 06-04-1998
WO 0151536	A	19-07-2001	AU 2201001 A CA 2395577 A1 CN 1423667 T EP 1252214 A1 WO 0151536 A1 JP 2003519631 T	24-07-2001 19-07-2001 11-06-2003 30-10-2002 19-07-2001 24-06-2003
WO 9841322	A	24-09-1998	US 5846897 A AT 258825 T AU 729058 B2 AU 6555098 A	08-12-1998 15-02-2004 25-01-2001 12-10-1998

INTERNATIONAL SEARCH REPORT

Internat Application No
PCT, no 03/05182

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9841322	A	CA 2266886 A1	24-09-1998
		DE 1021245 T1	19-04-2001
		EP 1163956 A1	19-12-2001
		EP 1021245 A1	26-07-2000
		JP 2001524142 T	27-11-2001
		WO 9841322 A1	24-09-1998
		US 5965686 A	12-10-1999